(12) **EUROPEAN PATENT SPECIFICATION**

(54) **Method for forming a thin film and apparatus for carrying out the method**

Verfahren zur Herstellung einer dünnen Schicht und Vorrichung zur Durchführung dieses Verfahrens

Procédé pour obtenir un film mince et appareillage pour la mise en oeuvre de ce procédé

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EP-A- 0 328 257   EP-A- 0 409 451
EP-A- 0 428 358   EP-A- 0 497 499
EP-A- 0 719 874   WO-A-94/18359

EP 0 945 523 B1

Description

[0001] The present invention relates to a method for forming a thin film of a composite metal compound as defined in the preamble of claim 1.

[0002] A method of this type is described in EP 719 874 A1. This reference describes a process of forming films of metallic compounds by sputtering ultra-thin films and transforming these films into one of a metallic compound by exposing it to a reactive gas plasma as it is. It is not disclosed to select the electrically neutral, activated species from the reactive gas, and it is not disclosed to invert the voltage from a negative value to a positive one.

[0003] EP 497 499 A1 describes a thin film coating method by means of an apparatus which includes a rotary cylindrical sputtering system which incorporates a separate deposition device and at least one chemical reaction device for simultaneously depositing materials and thereafter oxidising the deposited materials. The deposition devices are linear magnetron sputter cathode devices and the reaction device is a linear magnetron ion-source oxidiser device. It is not known described to select the electrically neutral activated species from the reactive gas nor is it described to invert the voltage applied to the target.

[0004] EP 428 358 A2 describes a magnetron sputtering apparatus, and particularly geometries and configurations therefor. The reference describes a thin film coating system using a plurality sequentially or simultaneously operated deposition and reaction zones and uses plasma that generates many ions from the used reactant gas (oxygen) for enhancing oxidation of the sputtered metals. Neither the use of electrically neutral activated species from the reactive gas nor the inversion of the voltage is disclosed in that reference.

[0005] EP 409 451 describes a process for depositing optical thin films by a rotary cylindrical sputtering system combining sputter deposition and reaction technology. It is not disclosed to select electrically neutral species from the reactive gas nor is it disclosed to invert the voltage within a specific interval from a positive range to a negative one.

[0006] EP 328 257 A2 describes a magnetron sputtering apparatus and process wherein reactive gas is applied to form adjacent the substrate a second plasma comprising ions of the reactive gas. This reference discloses neither to select the electrically neutral activated species from the reactive nor to invert the voltage from a negative range at a specific interval to a positive one.

[0007] The present invention relates to a method for forming a thin film of a composite metal compound and an apparatus for carrying out the method. More particularly, the invention relates to a method for forming through sputtering a thin film of a composite metal compound on a substrate in a stable manner and at a high rate of deposition.

[0008] Conventionally, when optical thin films for various groups of products are formed through use of only existing vapor deposition materials, satisfactory performances as required by the products are very difficult to obtain. That is, designing optical thin films through use of mere substances existing in the natural world has proved difficult in terms of attaining optical spectral characteristics as required by a certain group of products.

[0009] For example, configuration of wide-band antireflection films requires materials having an intermediate refractive index (between 1.46 and 2.20), which materials rarely exist in the natural world.

[0010] Generally, in order to decrease the reflectance of, for example, glass, over the entire wavelength range of visible light, glass must be coated with a vapor deposition material having a refractive index of 1.46-2.20, called an intermediate refractive index. Materials having an intermediate refractive index are limited, and the refractive index cannot be selected as desired. Accordingly, the following techniques are known as alternative techniques for obtaining an intermediate refractive index of the above-mentioned range.

[0011] (1) A low-refraction material (e.g. SiO_2 (refractive index: 1.46)) and a high-refraction material (e.g. TiO_2 (refractive index: 2.35)) are concurrently evaporated from respective evaporation sources, and an intermediate refractive index (1.46-2.40) is obtained by virtue of their mixing ratio; (2) a low-refraction material and a high-refraction material are concurrently evaporated from a single evaporation source in the form of a mixture, and an intermediate refractive index is obtained by virtue of their mixing ratio; (3) an intermediate refractive index is equivalently obtained through the combination of a low-refraction material and a high-refraction material (called the equivalent film technique); and (4) a composite target material is used in sputtering.

[0012] However, the above-mentioned techniques involve the following disadvantages.

[0013] In the above-mentioned technique (1), wherein a low-refraction material (e.g. SiO_2 (refractive index: 1.46)) and a high-refraction material (e.g. TiO_2 (refractive index: 2.35)) are concurrently evaporated from respective evaporation sources and an intermediate refractive index (1.46-2.40) is obtained by virtue of their mixing ratio, the stable deposition of a film through the simultaneous control of the rates of deposition from the two evaporation sources is difficult to achieve, and thus a desired refractive index is difficult to obtain with good reproducibility.

[0014] In the above-mentioned technique (2), wherein a low-refraction material and a high-refraction material are concurrently evaporated from a single evaporation source in the form of a mixture and an intermediate refractive index is obtained by virtue of their mixing ratio, when evaporation continues for a long period of time, the refractive index changes due to differences in melting point and vapor pressure between the low-refraction material and the high-refraction material. As a result, a desired refractive index is difficult to obtain stably.

[0015] In the above-mentioned technique (3), wherein an intermediate refractive index is obtained through use of an equivalent film formed from combined use of low-refraction and high-refraction materials, a given refractive index requires the formation of a very thin layer; thus, the control of film thickness becomes difficult and complicated.

[0016] As mentioned above, the conventional techniques fail to concurrently implement a high, stable deposition rate, a wide range of refractive index variation, and a simple control system.

[0017] An object of the present invention is to provide a method for forming a thin film of a composite metal compound by forming an ultra-thin film while subjecting the ultra-thin film to oxidation, nitriding, fluorination, or a like reaction, and forming on a substrate a thin film of a metallic compound having stable optical characteristics, dynamic characteristics, and like characteristics without increasing the substrate temperature and at a high rate of deposition.

[0018] Another development of the present invention is to provide a method for forming a thin film of a composite metal compound capable of obtaining a wide range of refractive index variation through use of a simple control system and to provide an apparatus for carrying out the same.

[0019] The above object is achieved by the method according to claim 1 of the present invention.

[0020] Herein, the expression "ultra-thin film" is used to discriminate a final thin film from a plurality of ultra-thin films which are deposited to become the final thin film, and denotes that each of the ultra-thin films is substantially thinner than the final thin film. The expression "activated species" refer to radicals, radicals in an excited state, atoms in an excited state, molecules in an excited state, and the like. A "radical" refers to an atom or molecule having at least one unpaired electron. An "excited state" denotes the state in which the energy level is higher as compared to the stable ground state having the lowest energy.

[0021] The method of the present invention will next be described in detail.

[0022] According to a main, first aspect of the present invention, there is provided a method for forming a thin film of a composite metal compound in which first, independent targets formed of at least two different metals are sputtered so as to form on a substrate an ultra-thin film of a composite metal or an incompletely-reacted composite metal. For example, one of two targets is formed of Si, while the other target is formed of Ta.

[0023] Next, the thus-formed ultra-thin film (e.g. Si + Ta) on the substrate is irradiated with the electrically neutral, activated species of a reactive gas (e.g. activated species of oxygen gas) so as to convert the composite metal or the incompletely-reacted composite metal to a composite metal compound (e.g. a composite of SiO_2 and Ta_2O_2) through reaction of the ultra-thin film with the activated species of the reactive gas. The

above-mentioned steps of forming an ultra-thin film and converting the ultra-thin film to a composite metal compound are sequentially repeated so as to form on a substrate a thin film of a composite metal compound having a desired thickness.

[0024] In a reactive film deposition step in which a composite metal compound is obtained from a composite metal or an incompletely-reacted composite metal, activated species are used for the following reason. For the chemical reaction in the film deposition step, chemically active, electrically neutral, activated species, such as radicals and excited species, are more decisively important than are charged particles, such as ions and electrons.

[0025] Activated species are generated through use of a plasma source for generating high-density plasma connected to a radio-frequency power source. Specifically, the plasma source is an inductively-coupled or capacitively-coupled plasma source having an external or internal coil, or a helicon wave plasma source. In order to obtain high-density plasma, a magnetic field of 20-300 gauss is generated in a plasma generation unit.

[0026] A voltage (usually a negative voltage) applied to each of the targets is inverted at 1-200 kHz intervals to a positive voltage ranging between +50 V and +200 V to thereby neutralize, with electrons in plasma, positive charges which accumulate in a compound to be formed on the surface, particularly an uneroded portion thereof, of each of the targets. Thus, through the temporary inversion to a positive voltage from a negative voltage, the positive-charged state on the surfaces of the targets is neutralized, so that the voltage of the targets can be held at a normal level.

[0027] FIGS. 4 to 6 show the relationship between electric power and optical characteristics, such as refractive index, absorption, heterogeneity, etc., for $Ta_xSi_yO_z$ films. In FIGS. 4 to 6, optical constants are calculated based on data regarding the spectral characteristics of a single-polarity film. As shown in FIG. 4, the refractive indices of $Ta_xSi_yO_z$ films vary with the ratio of the power applied to one guide to the power applied to the other guide.

[0028] As seen from FIG. 4, as the applied power ratio between the Si cathode and the Ta cathode increases, the refractive index decreases. Since the vapor deposition rate is fixed at 40 nm/min, the illustrated relationship between the refractive index and the applied power ratio holds. As a result, the minimum and maximum refractive indices at a wavelength of 550 nm are found 1.463 and 2.182, respectively. As the applied power ratio increases, the refractive index at a wavelength of 550 nm increases from 1.463 to 2.182. Also, the refractive index can be decreased from 2.182 to 1.463.

[0029] In deposition of a thin film of a composite metal compound having a desired thickness on a substrate as described above, when two metals are respectively sputtered through, for example, magnetron sputtering, any refractive index within the range between the refrac-

tive index intrinsic to one metal compound and the refractive index intrinsic to the other metal compound (e. g. the range between 1.46 and 2.25, wherein 1.46 is the refractive index of SiO_2, an Si compound, and 2.25 is the refractive index of Ta_2O_2, a Ta compound) can be imparted to the thin film through appropriate control of the power applied to the magnetron sputtering targets.

[0030] The film deposition process will next be described with reference to FIG. 3, which illustrates the process of forming a thin film of a composite metal compound on a substrate.

[0031] First, a substrate is placed in the position of a first metal target. The first metal target is sputtered so as to form a very thin metallic film (ultra-thin film) on the substrate. Then, the substrate is moved to the position of a second metal target. The second metal target is sputtered so as to form a very thin metallic film (ultra-thin film) on the substrate. As shown in FIG. 3, the first and second metals are homogeneously deposited on the substrate to form an ultra-thin film. That is, an ultra-thin film of a composite metal or an incompletely-reacted composite metal is formed on the substrate.

[0032] The thus-formed ultra-thin film is finally irradiated with the electrically neutral, activated species of a reactive gas so as to convert the composite metal or the incompletely-reacted composite metal to a composite metal compound through the reaction of the ultra-thin film with the activated species of the reactive gas. Specifically, the ultra-thin film is oxidized in the position of a radical source. The step of forming the ultra-thin film and the step of conversion to the composite metal compound are sequentially repeated so as to form on the substrate a thin film of the composite metal compound having a desired thickness.

[0033] In the present aspect, a substrate may be transferred or fixed so long as the step of forming an ultra-thin film and the step of conversion to a composite metal compound are sequentially repeated so as to form on the substrate a thin film of the composite metal compound having a desired thickness.

[0034] An apparatus for forming a thin film of a composite metal compound is provided comprising a vacuum chamber, film deposition process chambers, a reaction process chamber, and separation means (e.g. shield plates). In the film deposition process chambers, a working gas (e.g. argon gas) is introduced thereinto, and independent targets formed of at least two different metals (e.g. Si and Ta in the case of two different metals) are sputtered so as to form on a substrate an ultra-thin film of a composite metal or an incompletely-reacted composite metal.

[0035] In the reaction process chamber, the ultra-thin film (e.g. Si and Ta) formed in the film deposition process chambers is irradiated with the electrically neutral, activated species of a reactive gas (e.g. the activated species of oxygen) so as to convert the composite metal or the incompletely-reacted composite metal to a composite metal compound (e.g. SiO_2 and Ta_2O_2) through the

reaction of the ultra-thin film with the activated species of the reactive gas. The separation means is adapted to separate the reaction process chamber from the film deposition process chambers in terms of space and pressure by means of the shield plates.

[0036] The shield plates serving as the separation means define within the vacuum chamber separate spaces which serve as the reaction process chamber and the film deposition process chambers. That is, the thus-defined spaces within the vacuum chamber are not completely separated from each other, but maintain a substantially independent state so as to serve as the reaction process chamber and film deposition process chambers which can be controlled independently of each other. Thus, the reaction process chamber and the film deposition process chambers are configured to be least influential to each other so that optimum conditions can be established in each of the chambers.

[0037] Thus, the separation means prevents the reactive gas (e.g. the activated species of oxygen) from mixing with the working gas (e.g. argon gas) in the film deposition process chambers so that there can be sequentially repeated a stable film deposition process and a reaction process to thereby form on a substrate a thin film of a composite metal compound having a desired thickness.

[0038] The activated species of a reactive gas used in the reaction process chamber are electrically neutral radicals (atoms or molecules having at least one unpaired electron, or atoms or molecules in an excited state). Also, in the present invention, a magnetron sputtering device serve as a thin film deposition device.

[0039] Activated species are generated by means of: a radio-frequency discharge chamber comprising a quartz tube, around which a radio-frequency coil is wound; a radio-frequency power source for applying power to the radio-frequency coil via a matching box; reaction gas feed means for introducing a reactive gas from a gas cylinder into the radio-frequency discharge chamber via a mass flow controller; an external or internal coil for generating a magnetic field of 20-300 gauss within the radio-frequency discharge chamber; and a multi-aperture grid, a multi-slit grid, or a like grid disposed between the radio-frequency discharge chamber and the reaction process chamber.

[0040] A multi-aperture grid is formed of a metal or an insulator in which are formed a number of apertures having a diameter of 0.1-3 mm, and is cooled. A multi-slit grid is formed of a metal or an insulator in which are formed a number of slits having a width of 0.1-1 mm, and is cooled.

[0041] Preferably, a cooling measure, such as a water-cooling measure, is provided for the multi-aperture grid or multi-slit grid. The cooling measure may employ a known technique. Such a grid causes ions and electrons in plasma to mutually exchange charges on the surface of the grid to thereby introduce into the reaction process chamber only activated species which are re-

active and are not charged, i.e. which are electrically neutral.

[0042] As in the case of the first aspect, a voltage (usually a negative voltage) applied to each of the targets is inverted at 1-200 kHz intervals to a positive voltage ranging between +50 V and +200 V to thereby neutralize, with electrons in plasma, positive charges which accumulate in a compound to be formed on the surface, particularly an uneroded portion thereof, of each of the targets.

[0043] According to a further development of the present invention, there is provided a method for forming a thin film of a composite metal compound in which a thin film of a composite metal compound having a desired thickness is formed on a substrate in a manner similar to that described above and in which there is imparted to the thin film any refractive index within the range between the optical refractive index intrinsic to a constituent metal compound of the thin film and the optical refractive index intrinsic to another constituent metal compound of the thin film.

[0044] That is, the present aspect is characterized in that there is imparted to the thin film any refractive index within the range between the optical refractive index intrinsic to a constituent metal compound of a thin film of a composite metal compound and the optical refractive index intrinsic to another constituent metal compound of the thin film.

[0045] As described in the section of the first aspect with reference to FIG. 3, Si serving as a first metal and Ta serving as a second metal, for example, are sputtered, and the aforementioned film deposition process is repeated to form a composite oxide film.

[0046] Through the control of the magnitude of power applied to the first metal target and that of power applied to the second metal target, the refractive index of a thin film can be varied. For example, as shown in FIG. 4, the refractive index of a thin film varies with the ratio between the power applied to Si serving as the first metal and the power applied to Ta serving as the second metal. Accordingly, through the continuous variation of the power applied to the two targets according to a predetermined rule, a refractively gradient film can be formed.

[0047] As in the cases described above, the electrically neutral, activated species of a reactive gas are radicals (atoms or molecules having at least one unpaired electron, or atoms or molecules in an excited state). Also, the above-mentioned sputtering is magnetron sputtering. Further, a voltage (usually a negative voltage) applied to each of the targets is inverted at 1-200 kHz intervals to a positive voltage ranging between +50 V and +200 V to thereby neutralize, with electrons in plasma, positive charges which accumulate in a compound to be formed on the surface, particularly an uneroded portion thereof, of each of the targets.

[0048] An apparatus for forming a thin film of a composite metal compound is provided, comprising the features described above and transfer means for sequentially and repeatedly transferring a substrate between thin film deposition portions for forming a thin film through sputtering, which thin film deposition portions correspond to the aforementioned film deposition process chambers, and an exposure-to-radicals portion for exposing a thin film to radicals of a reactive gas emitted from a radical source, which exposure-to-radicals portion corresponds to the aforementioned reaction process chamber. A thin film of a composite metal compound is formed on the substrate through the sequentially repeated transfer of the substrate between the thin-film-deposition portions and the exposure-to-radicals portion. Also, there is imparted to the thin film any refractive index within the range between the optical refractive index intrinsic to a constituent metal compound of a thin film of a composite metal compound and the optical refractive index intrinsic to another constituent metal compound of the thin film.

[0049] A substrate is held by an electrically-insulated substrate holder so as to prevent the occurrence of an unusual discharge on the substrate. As in the cases described above, the activated species of a reactive gas used in the reaction process chamber are electrically neutral radicals (atoms or molecules having at least one unpaired electron, or atoms or molecules in an excited state); a magnetron sputtering device serves as a film deposition device; and a negative voltage applied to each of the targets is inverted at 1-200 kHz intervals to a positive voltage ranging between +50 V and +200 V to thereby neutralize, with electrons in plasma, positive charges which accumulate in a compound to be formed on the surface, particularly an uneroded portion thereof, of each of the targets. Also, a mechanism of the generation of the activated species, a grid, and shield means are similar to those of the preceding aspects.

[0050] According to a further development of the present invention, a thin film of a composite metal compound is formed on a substrate in a manner similar to that of the first aspect, and any optical characteristics are imparted to the thin film through the continuous variation of the refractive index of the thin film in the direction of the thickness of the thin film within the range between the optical refractive index intrinsic to a constituent metal compound of the thin film and the optical refractive index intrinsic to another constituent metal compound of the thin film.

[0051] Next will be described, as examples, a 3-layer antireflection film having an intermediate-refractive-index layer and a 2-layer antireflection film having a refractively gradient layer. Their film configurations are, for example, as follows:

(1) substrate/M(λ/4)/2H(λ/2)/L(λ/4)/air; and
(2) substrate/G/L(λ/4)/air (G: refractively gradient layer).

[0052] In this case, the refractive index of the intermediate-refractive-index layer M is represented by

$n_m = n_1\sqrt{n_s}$, where n_m is the refractive index of the intermediate-refractive-index layer M, n_1 is the refractive index of the low-refractive-index layer, and n_s is the refractive index of the substrate. The 2-layer antireflection film is designed based on the conventional 2-layer antireflection design called w-coat; specifically substrate/2H(λ/2)/L(λ/4)/air. FIG. 7 shows the calculated and measured spectral curves of the 3-layer and 2-layer antireflection films. As seen from FIG. 7, the calculated values and the measured values are in good coincidence. In the case of the 2-layer antireflection film, the high-refractive-index layer of the conventional w-coat is replaced by a refractively gradient layer, thereby expanding the range of antireflection.

[0053] As mentioned above, through the continuous variation of the refractive index of a thin film in the direction of the thickness of the thin film, any optical characteristics can be imparted to the thin film.

[0054] In the above-described aspects, two sputterers are used for sputtering two kinds of metals. However, three or more sputterers may be used. Such a configuration is feasible because the film deposition process chambers and the reaction process chamber are separated from each other by the shield means and can be controlled independently.

[0055] Thus, the present invention yields the following advantages: the refractive index can be controlled to any value within the range between the respective refractive indices intrinsic to a plurality of metals to be sputtered; an ultra-thin film can be formed while the ultra-thin film is undergoing oxidation, nitriding, fluorination, or a like reaction; and a thin film of a metallic compound having stable optical characteristics, dynamic characteristics, and like characteristics can be formed on a substrate without increasing the substrate temperature and at a high rate of deposition. Also, a wide range of refractive index variation can be obtained through use of a simple control system.

FIG. 1 is a schematic view showing an apparatus for forming a thin film;
FIG. 2 is a schematic side view as viewed along the line A-B-C of FIG. 1;
FIG. 3 is an explanatory view showing the process of forming a thin film of a composite metal compound on a substrate;
FIG. 4 is a graph showing the relation between power ratio and refractive index;
FIG. 5 is a graph showing the relation between extinction coefficient and refractive index;
FIG. 6 is a graph showing the relation between heterogeneity and refractive index for a plurality of thin films; and
FIG. 7 is a graph showing the relation between reflectance and wavelength for comparison between calculated values and experimental values.

[0056] An embodiment of an apparatus S performing the method for forming a thin film according to the present invention includes a vacuum chamber 11, a film deposition process chambers 20 and 40, a reaction process chamber 60, shield plates 31, 51, and 75 (which serve as separation means or shield means), a substrate holder 13 and drive means thereof (which serve as transfer means), and means for generating activated species.

[0057] The vacuum chamber 11 is formed of a closed hollow container having any shape. The substantially cylindrical substrate holder 13 is disposed at the center of the vacuum chamber 11 in a manner rotatable at a predetermined speed. The film deposition process chambers 20 and 40 and the reaction process chamber 60 are disposed around the substrate holder 13 and within the vacuum chamber 11.

[0058] The film deposition process chambers 20 and 40 are enclosed with the shield plates 31 and 51, respectively, independently of each other, and have at least two sputterers.

[0059] The film deposition process chambers 20 and 40 are disposed opposite to each other with respect to the substrate holder 13. The film deposition process chambers 20 and 40 are defined by the shield plates 31 and 51, respectively.

[0060] The shield plates 31, 51, and 75 define separate spaces which serve as the film deposition process chambers 20 and 40 and the reaction process chamber 60 (which will be described later), respectively, in a vacuum atmosphere established within the vacuum chamber 11. The thus-defined spaces are not completely separated from each other, but are substantially independent of each other and serve as the film deposition process chambers 20 and 40 and the reaction process chamber 60, which are independently controllable.

[0061] Accordingly, the film deposition process chambers 20 and 40 and the reaction process chamber 60 are configured to be least influential to each other so that optimum conditions can be established in each of the chambers 20, 40, and 60. Preferably, the pressure of the film deposition process chambers 20 and 40 is set higher than that of the reaction process chamber 60.

[0062] Such pressure setting prevents a reactive gas (e.g. oxygen gas) in the reaction process chamber 60 from entering the film deposition process chambers 20 and 40. Thus, there can be prevented the occurrence of an unusual discharge which would otherwise result due to the formation of a metallic compound on the surfaces of targets 29 and 49. For example, the pressure (the degree of vacuum) of the film deposition process chambers 20 and 40 is preferably $0.8\text{-}10 \times 10^{-3}$ Torr, and the pressure (the degree of vacuum) of the reaction process chamber 60 is preferably $0.5\text{-}8 \times 10^{-3}$ Torr, thereby establishing the condition that the pressure of the film deposition process chambers 20 and 40 is greater than that of the reaction process chamber 60.

[0063] The film deposition process chambers 20 and 40 have sputtering electrodes 21 and 41, respectively.

Spaces in front of the sputtering electrodes 21 and 41 serve as sputtering film deposition portions.

[0064] The film deposition process chambers 20 and 40 are connected to sputtering gas cylinders 27 and 47 via mass flow controllers 25 and 45, respectively. A sputtering gas, such as argon, is introduced from the cylinders 27 and 47 into the film deposition process chambers 20 and 40, respectively, to thereby establish a regulated sputtering atmosphere within the film deposition process chambers 20 and 40. Through the application of power from sputtering power sources 23 and 43, sputtering is performed. In the present embodiment, a low-refraction material is used as the target 29. Examples of such a low-refraction material include Si. Also, a high-refraction material is used as the target 49. Examples of such a high-refraction material include Ti, Zr, Ta, and Nb.

[0065] The reaction process chamber 60 includes an activated-species generator 61, which serves as a radical source, for generating the activated species of a reactive gas and a grid 62. The grid 62 may be a multi-aperture grid or a multi-slit grid.

[0066] The activated-species generator 61 may be an inductively-coupled type, a capacitively-coupled type, or a inductively, capacitively-coupled type and has an external or internal electrodes.

[0067] The activated-species generator 61 includes a radio-frequency (RF) discharge chamber 63 formed of a quartz tube and a radio-frequency (RF) coil wound on the RF discharge chamber 63. A radio-frequency (RF) power source 69 applies power (a high-frequency power of 100 kHz to 50 MHz) to the RF coil 65 via a matching box 67. At the same time, a reactive gas, such as oxygen gas, is introduced from a reactive gas cylinder 73 into the RF discharge chamber 63 via a mass flow controller 71. As a result, the plasma of the reactive gas is generated. Examples of such a reactive gas include oxidizing gases such as oxygen and ozone, nitriding gases such as nitrogen, carbonating gases such as methane, and fluorinating gases such as CF_4.

[0068] In order to obtain a high-density plasma, a magnetic field of 20-300 gauss is generated within the quartz tube through use of the external coil 80 or the internal coil 81. The grid 62 disposed at the connecting portion between the quartz tube and the vacuum chamber 11 is adapted to release only activated species into the reaction process chamber 60.

[0069] The multi-aperture grid serving as the grid 62 is formed of a metal or an insulator in which are formed a number of apertures having a diameter of 0.1-3 mm, and is cooled. The multi-slit grid serving as the grid 62 is formed of a metal or an insulator in which are formed a number of slits having a width of 0.1-1 mm, and is cooled.

[0070] Through use of the grid 62, there are selectively introduced into the reaction process chamber 60 the activated species of a reactive gas, i.e. radicals, radicals in an excited state, atoms in an excited state, and mol-

ecules in an excited state, while charged particles such as electrons and ions cannot pass through the grid 62 and thus cannot enter the reaction process chamber 60. Accordingly, in the reaction process chamber 60, a metallic ultra-thin film is not exposed to the above-mentioned charged particles, but is exposed only to electrically neutral activated species of a reaction gas and reacts with the activated species to thereby be converted from a metallic thin film of Si and Ta or the like to a thin film of a composite metal compound (SiO_2 and Ta_2O_2).

[0071] The transfer means of the present embodiment is adapted to sequentially and repeatedly transfer a substrate between thin film deposition portions for forming a thin film through sputtering, which thin film deposition portions correspond to the film deposition process chambers 20 and 40, and an exposure-to-radicals portion for exposing a thin film to radicals of a reactive gas emitted from a radical source, which exposure-to-radicals portion corresponds to the reaction process chamber 60.

[0072] The transfer means of the present embodiment will now be described specifically. As shown in FIGS. 1 and 2, the substantially cylindrical substrate holder 13 serving as the transfer means is disposed at the center of the vacuum chamber 11 in a manner rotatable at a predetermined speed. The substrate holder 13 is rotatably supported by unillustrated bearing portions in the vacuum chamber 11. The bearing portions may be formed inside or outside the vacuum chamber 11. The substrate holder 13 is connected to the output shaft of a rotational drive 17 (motor) and rotated by the rotating output shaft.

[0073] The rotational drive 17 is configured such that the rotational speed thereof can be controlled. A substrate (not shown) is mounted on the substrate holder 13 and transferred sequentially and repeatedly between the thin film deposition portions for forming a thin film through sputtering in the film deposition process chambers 20 and 40 and the exposure-to-radicals portion for exposing a thin film to radicals of a reactive gas emitted from the radical source in the reaction process chamber 60.

EXAMPLES

[0074] Sputtering conditions and conditions for generating the activated species of a reactive gas are as follows:

(1) Sputtering conditions (Si)

Applied power: 0-2.8 kW
Substrate temperature: room temperature
Argon flux: 300 sccm
Rotational speed of substrate holder: 100 rpm
Thickness of ultra-thin film: 2-6 angstroms

(2) Sputtering conditions (Ta)

Applied power: 0-1.5 kW
Substrate temperature: room temperature
Argon flux: 200 sccm
Rotational speed of substrate holder: 100 rpm
Thickness of ultra-thin film: 1-4 angstroms

(3) Conditions for generating radicals of reactive gas (O_2)

Applied power: 2.0 kW
Oxygen flux: 60 sccm

[0075] In order to describe the present invention, there will next be described, by way of example, the case where a thin film of a composite metal compound of SiO_2 and Ta_2O_2 is deposited under the above sputtering conditions and conditions for generating the activated species of a reactive gas.

[0076] Silicon (Si) is sputtered in the steps of: fixing silicon serving as the target 29 in place; introducing argon gas into the film deposition process chamber 20 from the sputtering gas cylinder 27; and applying power to the target 29 from the sputtering power source 23. Tantalum (Ta) is sputtered in the steps of: fixing tantalum serving as the target 29 in place; introducing argon gas into the film deposition process chamber 40 from the sputtering gas cylinder 47; and applying power to the target 29 from the sputtering power source 43.

[0077] A refractive index to be obtained depends on the ratio between the power applied to one magnetron sputtering target and the power applied to the other magnetron sputtering target in FIG. 3. Oxygen gas is introduced into the activated-species generator 61 from the reactive gas cylinder 73, and the activated-species generator 61 is activated, thereby generating the activated species of oxygen gas (oxygen atoms).

[0078] As the substrate holder 13 carrying a substrate is rotated by the rotational drive 17 (motor), an Si ultra-thin film is deposited on the substrate when the substrate is located in front of the sputtering electrode 21 (the sputtering thin-film deposition portion) in the film deposition process chamber 20. Next, a Ta ultra-thin film is deposited on the substrate when the substrate is located in front of the sputtering electrode 41 (the sputtering thin-film deposition portion) in the film deposition process chamber 40. The thus-formed thin film of the composite metal is oxidized by the activated species of oxygen gas when the substrate is located in front of the grid 62 (the exposure-to-radicals portion) in the reaction process chamber 60. As a result, the thin film of the composite metal is converted to a thin film of a composite metal compound of SiO_2 and Ta_2O_2.

[0079] The substrate holder 13 carrying the substrate is rotated so as to repeat the deposition of an ultra-thin film of Si and Ta and the conversion of the ultra-thin film of Si and Ta to a thin film of a composite compound of SiO_2 and Ta_2O_2 until a thin film of a composite compound of SiO_2 and Ta_2O_2 having a desired thickness is

obtained.

[0080] Spaces in front of the sputtering electrodes 21 and 41 are enclosed by the shield plates 31 and 51, respectively, and a space in front of the grid 62 is enclosed by the shield plates 75. A sputtering gas is introduced into the corresponding enclosed spaces from the sputtering gas cylinders 27 and 47, and a reaction gas is introduced into the corresponding enclosed space from the reaction gas cylinder 73. The thus-introduced gases are evacuated into an evacuation system by a vacuum pump 15. Accordingly, the sputtering gas does not enter the space enclosed by the shield plates 75, or the reactive gas does not enter the spaces enclosed by the shield plates 31 and 51.

[0081] Also, discharge associated with magnetron sputtering and discharge associated with the generation of the activated species of a reaction gas can be controlled independently of each other to thereby have no effect on each other, and thus are performed stably, thereby avoiding the occurrence of an unexpected accident and providing a high reliability. Further, since the activated-species generator 61 is configured not to expose a substrate to plasma, the substrate is free from various damages which would otherwise result due to charged particles. Also, the substrate temperature can be controlled to 100°C or lower to thereby avoid an unfavorable temperature rise. In the case of a plastic substrate, since the substrate temperature does not exceed 100°C, a glass transition point is not exceeded during sputtering. Thus, the plastic substrate does not suffer deformation or like damage.

[0082] The above-mentioned phenomena will now be described with reference to FIGS. 4 to 7. FIGS. 4 to 7 show the relation among power and optical characteristics, such as refractive index, extinction coefficient, and heterogeneity, of $Ta_xSi_yO_z$. Optical constants are calculated based on data regarding the spectral characteristics of a single-polarity film. As shown in FIG. 4, the refractive indices of $Ta_xSi_yO_z$ films vary with the ratio of the power applied to one guide to the power applied to the other guide. As seen from FIG. 4, as the applied power ratio between the Si cathode and the Ta cathode increases, the refractive index decreases.

[0083] Since the vapor deposition rate is fixed at 40 nm/min, the illustrated relationship between the refractive index and the applied power ratio holds. As a result, the minimum and maximum refractive indices at a wavelength of 550 nm are found 1.463 and 2.182, respectively. As the applied power ratio increases, the refractive index at a wavelength of 550 nm increases from 1.463 to 2.182. Also, the refractive index can be decreased from 2.182 to 1.463.

[0084] FIG. 5 shows the relation between extinction coefficient and refractive index, and FIG. 6 shows the relation between heterogeneity and refractive index for a plurality of thin films. As shown in FIG. 5, the extinction coefficients of thin films having a refractive index of 1.463 to 2.00 at a wavelength of 550 nm are smaller

than 5×10^{-4}. The extinction coefficients of thin films having a refractive index of 2.00 to 2.182 are smaller than 1×10^{-3}. As seen from FIG. 6, the thin films show a very small heterogeneity. Thin films having a refractive index not higher than 2.00 are negatively heterogeneous. Thin films having a refractive index higher than 2.00 are positively heterogeneous.

[0085] Based on the above findings, a 3-layer antireflection film having an intermediate-refractive-index layer and a 2-layer antireflection film having a refractively gradient layer were designed and fabricated. The fabricated film configurations were as follows:

(1) substrate/M(λ/4)/2H(λ/2)/L(λ/4)/air; and
(2) substrate/G/L(λ/4)/air (G: refractively gradient layer).

[0086] The refractive index of the intermediate-refractive-index layer M is represented by $n_m = n_1\sqrt{n_s}$, where n_m is the refractive index of the intermediate-refractive-index layer M, n_1 is the refractive index of the low-refractive-index layer, and n_s is the refractive index of the substrate. The 2-layer antireflection film was designed based on the conventional 2-layer antireflection design called w-coat; specifically substrate/2H(λ/2)/L(λ/4)/air. FIG. 7 shows the calculated and measured spectral curves of the 3-layer and 2-layer antireflection films. As seen from FIG. 7, the calculated values and the measured values are in good coincidence. In the case of the 2-layer antireflection film, the high-refractive-index layer of the conventional w-coat was replaced by a refractively gradient layer, thereby expanding the range of antireflection.

[0087] The present invention includes the following embodiments:

- An apparatus for forming a thin film of a composite metal compound, wherein the multi-aperture grid is formed of a metal or an insulator in which are formed a number of apertures having a diameter of 0.1-3 mm, and is cooled.
- An apparatus for forming a thin film of a composite metal compound, wherein the multi-slit grid is formed of a metal or an insulator in which are formed a number of slits having a width of 0.1-1 mm, and is cooled.
- A method for forming a thin film of a composite metal compound comprising the steps of: sputtering at least two independent different metals so as to form on a substrate an ultra-thin film of a composite metal or an incompletely-reacted composite metal; and irradiating the ultra-thin film with the electrically neutral, activated species of a reactive gas so as to convert the composite metal or the incompletely-reacted composite metal to a composite metal compound through the reaction of the ultra-thin film with the activated species of the reactive gas, wherein the step of forming the ultra-thin film and the step

of conversion to the composite metal compound are sequentially repeated so as to form on the substrate a thin film of the composite metal compound having a desired thickness, and wherein there is imparted to the thin film any refractive index within the range between the optical refractive index intrinsic to a constituent metal compound of the thin film and the optical refractive index intrinsic to another constituent metal compound of the thin film through the continuous variation of the refractive index of the thin film in the direction of the thickness of the thin film.

Claims

1. A method for forming a thin film of a composite metal compound comprising the steps of:

   magnetron sputtering independent targets (29, 49) formed of at least two different metals so as to form on a substrate an ultra-thin film of a composite metal or an incompletely-reacted composite metal;
   irradiating the ultra-thin film with the activated species of a reactive gas so as to convert the composite metal or the incompletely-reacted composite metal to a composite metal compound through the reaction of the ultra-thin film with the activated species of the reactive gas;
   sequentially repeating the step of forming the ultra-thin film and the step of conversion to the composite metal compound so as to form on the substrate a thin film of the composite metal compound having a desired thickness, **characterised in that** the step of irradiating includes the step of selecting the electrically neutral, activated species from the reactive gas and irradiating the ultra-thin films with the electrically neutral, activated species of the reactive gas, and that a negative voltage applied to each of the targets (29, 49) is inverted at 1-200 kHz intervals to a positive voltage ranging between + 50 V and + 200 V to thereby neutralise, with electrons in plasma, positive charges which accumulate in a compound to be formed on the surface of each of the targets (29, 49).

2. A method according to claim 1, wherein the electrically neutral, activated species of the reactive gas are radicals selected from the group consisting of atoms having at least one unpaired electron, molecules having at least one unpaired electron, atoms in an excited state, and molecules in an excited state.

3. A method for forming a thin film of a composite metal compound according to claim 1 or 2, wherein the thin film is formed to have any refractive index within

the range between the optical refractive index intrinsic to a constituent metal compound of the thin film and the optical refractive index intrinsic to another constituent metal compound of the thin film.

4. A method according to any one of claims 1 to 3, wherein the activated species are generated by means of:

> a radio-frequency discharge chamber (63) comprising a quartz tube and a radio-frequency coil (65) wound onto the quartz tube;
> a radio frequency power source (69) for applying power to the radio-frequency coil (65) via a matching box (67);
> reaction gas feed means for introducing a reactive gas from a gas cylinder (73) into the radio-frequency discharge chamber (63) via a mass flow controller (71);
> an external or internal coil (80, 81) for generating a magnetic field of 20-300 gauss within the radio-frequency discharge chamber (63); and
> a multi-aperture grid (62) or a multi-slit grid (62) disposed between the radio-frequency discharge chamber (63) and said reaction process chamber (60).

5. A method according to any one of claims 1 to 4, wherein said substrate is held by an electrically-insulated substrate holder (13) so as to prevent the occurrence of an unusual discharge on said substrate.

6. A method according to any one of claims 1 to 5, wherein for one of the targets (29, 49) a low-refraction material and for another of the targets (49, 29) a high-refraction material is used.

7. A method according to claim 4, wherein said multi-aperture grid (62) is formed of a metal or an insulator in which are formed a number of apertures having a diameter of 0.1-3 mm, and is cooled.

8. A method according to claim 5, wherein said multi-slit grid (62) is formed of a metal or an insulator in which are formed a number of slits having a width of 0.1-1 mm, and is cooled.

Patentansprüche

1. Verfahren zum Bilden eines dünnen Films einer Komposit-Metall-Verbindung, aufweisend die Schritte:

> Magnetron-Sputtern unabhängiger Targets (29, 49), gebildet aus mindestens zwei unterschiedlichen Metallen, um so auf einem Substrat einen ultra-dünnen Film eines Komposit-Metalls oder eines nicht vollständig reagierten Komposit-Metalls zu bilden;
> Bestrahlen des ultra-dünnen Films mit den aktivierten Spezies eines reaktiven Gases, um so das Komposit-Metall oder das nicht vollständig reagierte Komposit-Metall zu einer Komposit-Metall-Verbindung über die Reaktion des ultra-dünnen Films mit den aktivierten Spezies des reaktiven Gases umzuwandeln;
> sequenzielles Wiederholen des Schritts eines Bildens des ultra-dünnen Films und des Schritts eines Umwandelns zu der Komposit-Metall-Verbindung, um so auf dem Substrat einen dünnen Film der Komposit-Metall-Verbindung zu bilden, der eine erwünschte Dicke besitzt,

dadurch gekennzeichnet, dass der Schritt eines Bestrahlens den Schritt eines Auswählens der elektrisch neutralen, aktivierten Spezies von dem reaktiven Gas und eines Bestrahlens der ultra-dünnen Filme mit den elektrisch neutralen, aktivierten Spezies des reaktiven Gases umfasst, und dass eine negative Spannung, angelegt an jedes der Targets (29, 49), unter Intervallen von 1-200 kHz zu einer positiven Spannung invertiert wird, die von +50 V bis +200 V reicht, um dadurch, mit Elektronen in einem Plasma, positive Ladungen zu neutralisieren, die sich in einer Verbindung ansammeln, die auf der Oberfläche jedes der Targets (29, 49) gebildet wird.

2. Verfahren nach Anspruch 1, wobei die elektrisch neutralen, aktivierten Spezies des reaktiven Gases Radikale sind, ausgewählt aus der Gruppe, die aus Atomen, die mindestens ein nicht gepaartes Elektron haben, Molekülen, die mindestens ein ungepaartes Elektron haben, Atomen in einem angeregten Zustand und Molekülen in einem angeregten Zustand, besteht;

3. Verfahren zum Bilden eines dünnen Films einer Komposit-Metall-Verbindung nach Anspruch 1 oder 2, wobei der dünne Film so gebildet ist, um irgendeinen Brechungsindex innerhalb des Bereichs zwischen dem optischen Brechungsindex, der einem Metall-Verbindungs-Bestandteil des dünnen Films eigen ist, und dem optischen Brechungsindex, der einen anderen Metall-Verbindungs-Bestandteil des dünnen Films eigen ist, zu haben.

4. Verfahren nach einem der Ansprüche 1 bis 3, wobei die aktivierten Spezies erzeugt werden mittels:

> einer Hochfrequenz-Entladungskammer (63), die ein Quarzrohr und eine Hochfrequenzspule (65), gewickelt auf dem Quarzrohr, aufweist;
> einer Hochfrequenz-Energiequelle (69) zum

Anlegen von Energie an die Hochfrequenzspu-
le (65) über eine Anpassungsbox (67);
einer Reaktionsgas-Zuführeinrichtung zum
Einführen eines reaktiven Gases von einem
Gaszylinder (73) in die Hochfrequenz-Entla-
dungskammer (63) über eine Massenfluss-Re-
geleinrichtung (71);
einer externen oder internen Spule (80, 81)
zum Erzeugen eines magnetischen Felds mit
20-300 Gauss innerhalb der Hochfrequenz-
Entladungskammer (63); und
einem Multi-Apertur-Gitter (62) oder einem
Multi-Schlitz-Gitter (62), angeordnet zwischen
der Hochfrequenz-Entladungskammer (63)
und der Reaktionsprozesskammer (60).

5. Verfahren nach einem der Ansprüche 1 bis 4, wobei
das Substrat durch einen elektrisch isolierten Sub-
strathalter (13) so gehalten ist, um das Auftreten ei-
ner ungewöhnlichen Entladung auf dem Substrat zu
verhindern.

6. Verfahren nach einem der Ansprüche 1 bis 5, wobei
für eines der Targets (29, 49) ein niedrig brechen-
des Material und für ein anderes der Targets (49,
29) ein hoch brechendes Material verwendet wird.

7. Verfahren nach Anspruch 4, wobei das Multi-Aper-
tur-Gitter (62) aus einem Metall oder einem Isolator
gebildet ist, in dem eine Anzahl von Aperturen ge-
bildet ist, die einen Durchmesser von 0,1-3 mm ha-
ben, und gekühlt wird.

8. Verfahren nach Anspruch 5, wobei das Multi-
Schlitz-Gitter (62) aus einem Metall oder einem Iso-
lator gebildet ist, in dem eine Anzahl von Schlitzen
gebildet ist, die eine Breite von 0,1-1 mm haben,
und gekühlt wird.

Revendications

1. Procédé pour former un film mince d'un composé
métallique composite comprenant les étapes con-
sistant à :

pulvériser par magnétron des cibles indépen-
dantes (29, 49) constituées d'au moins deux
métaux différents de manière à former sur un
substrat un film ultramince d'un métal compo-
site ou d'un métal composite dont la réaction
est incomplète ;
irradier le film ultramince avec les espèces ac-
tivées d'un gaz réactif de manière à convertir
le métal composite ou le métal composite dont
la réaction est incomplète en un composé mé-
tallique composite par la réaction du film ultra-
mince avec les espèces activées du gaz

réactif ;
répéter de manière séquentielle l'étape de for-
mation du film ultramince et l'étape de conver-
sion du composé métallique composite de ma-
nière à former sur le substrat un film mince du
composé métallique composite d'une épais-
seur souhaitée,

caractérisé en ce que l'étape d'irradiation
comprend l'étape consistant à sélectionner les es-
pèces activées électriquement neutres du gaz réac-
tif et à irradier les films ultraminces avec les espè-
ces activées électriquement neutres du gaz réactif,
et **en ce qu'**une tension négative appliquée à cha-
cune des cibles (29, 49) est inversée à des fréquen-
ces de 1 à 200 kHz en une tension positive compri-
se entre +50 V et +200 V afin, de ce fait, de neutra-
liser, par les électrons du plasma, les charges po-
sitives accumulées dans un composé devant être
formé sur la surface de chacune des cibles (29, 49).

2. Procédé selon la revendication 1, dans lequel les
espèces activées électriquement neutres du gaz
réactif sont des radicaux sélectionnés dans le grou-
pe consistant en des atomes comportant au moins
un électron non apparié, des molécules comportant
au moins un électron non apparié, des atomes dans
un état excité et des molécules dans un état excité.

3. Procédé pour former un film mince d'un composé
métallique composite selon la revendication 1 ou 2,
dans lequel le film mince est formé pour présenter
n'importe quel indice de réfraction dans la gamme
entre l'indice de réfraction optique intrinsèque d'un
composé métallique constitutif du film mince et l'in-
dice de réfraction optique intrinsèque d'un autre
composé métallique constitutif du film mince.

4. Procédé selon l'une quelconque des revendications
1 à 3, dans lequel les espèces activées sont géné-
rées au moyen :

d'une chambre de décharge radiofréquence
(63) comprenant un tube de quartz et une bo-
bine radiofréquence (65) enroulée sur le tube
de quartz ;
d'une source de puissance radiofréquence (69)
pour appliquer une puissance à la bobine ra-
diofréquence (65) par l'intermédiaire d'une boî-
te d'adaptation (67) ;
de moyens d'alimentation en gaz de réaction
pour introduire un gaz réactif provenant d'une
bouteille de gaz (73) dans la chambre de dé-
charge radiofréquence (63) par l'intermédiaire
d'un contrôleur de débit massique (71) ;
d'une bobine externe ou interne (80, 81) pour
générer un champ magnétique de 20 à 300
gauss à l'intérieur de la chambre de décharge

radiofréquence (63) ; et
d'une grille à ouvertures multiples (62) ou d'une
grille à fentes multiples (62) disposée entre la
chambre de décharge radiofréquence (63) et
ladite chambre de traitement de réaction (60).

5. Procédé selon l'une quelconque des revendications
1 à 4, dans lequel ledit substrat est maintenu par un
support de substrat isolé électriquement (13) de
manière à éviter l'apparition d'une décharge inha-
bituelle sur ledit substrat.

6. Procédé selon l'une quelconque des revendications
1 à 5, dans lequel, pour une des cibles (29, 49), un
matériau à faible réfraction est utilisé et, pour une
autre des cibles (49, 29), un matériau à haute ré-
fraction est utilisé.

7. Procédé selon la revendication 4, dans lequel ladite
grille à ouvertures multiples (62) est réalisée en un
métal ou un isolant dans lequel sont formées un cer-
tain nombre d'ouvertures présentant un diamètre
de 0,1 à 3 mm, et est refroidie.

8. Procédé selon la revendication 5, dans lequel ladite
grille à fentes multiples (62) est réalisée en un métal
ou un isolant dans lequel sont formées un certain
nombre de fentes présentant une largeur de 0,1 à
1 mm, et est refroidie.

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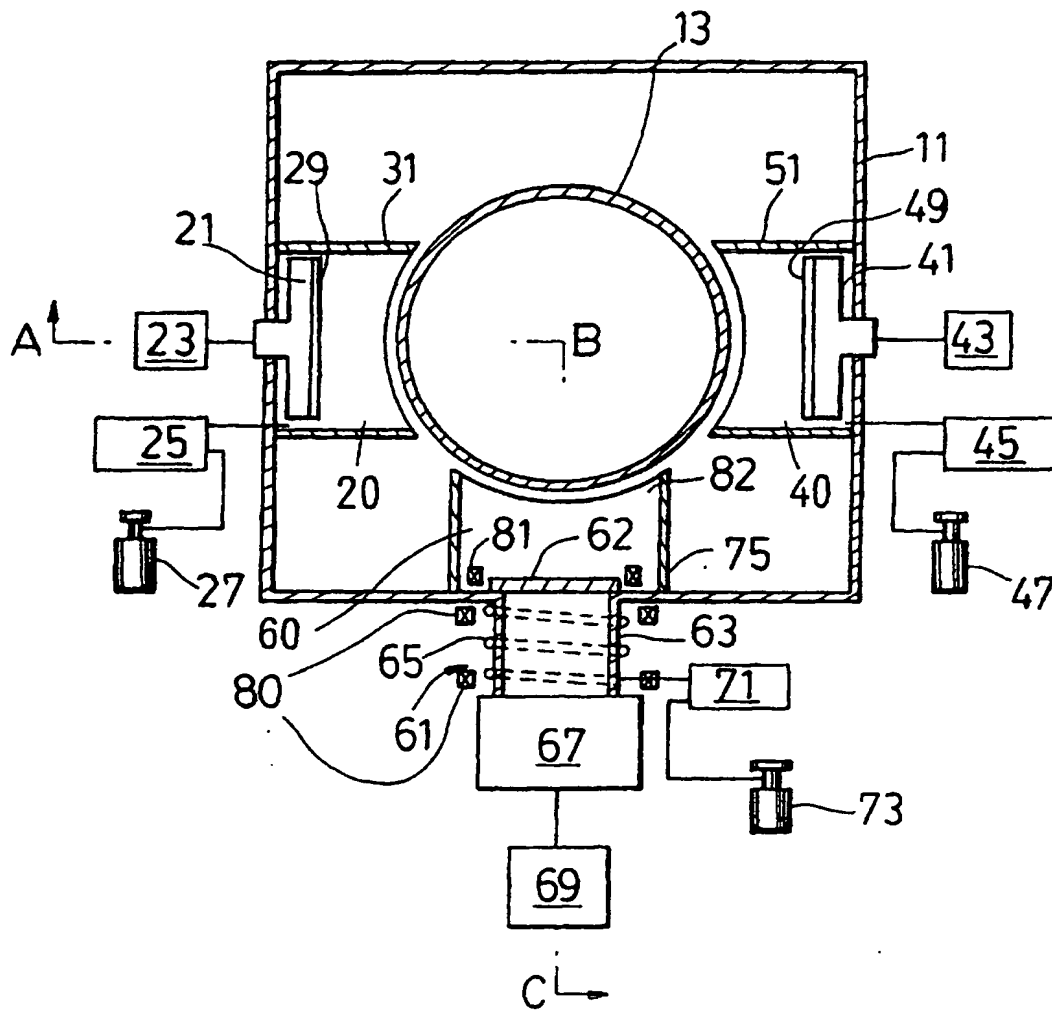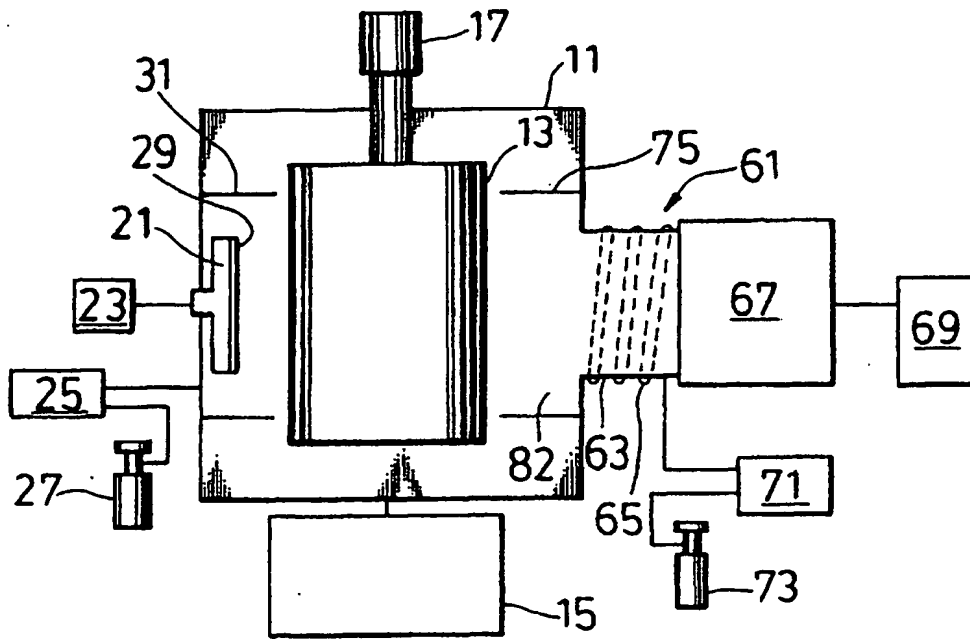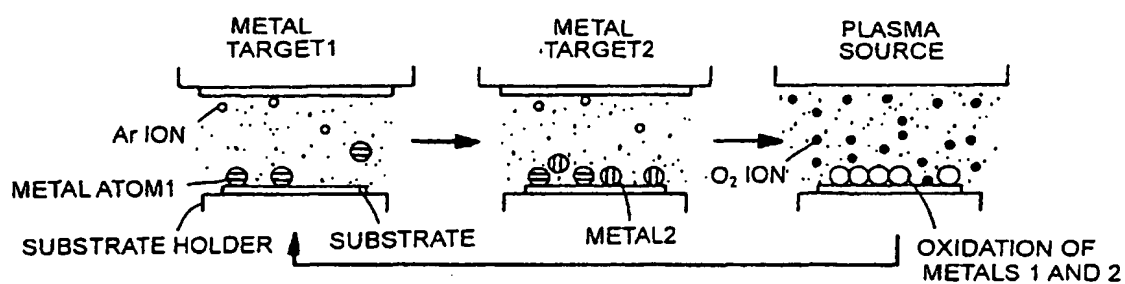35

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Fig.1

Fig.2

Fig.3

Fig.4

$$y = 1.55x^3 - 2.56x^2 + 0.28x + 2.18$$

Fig.5

Fig.6

Fig.7